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(57) Abstract

The invention relates to a process for the manufacture of an object with a coloured marking by irradiating the surface of the object with laser light in the form of the marking, wherein at least at the place where the marking is applied the object consists of a plastic composition comprising at least three prechrome compounds which only acquire their colour-generating capacity after a colour-generating treatment and which under the influence of laser light can lose their colour-generating capacity again, the surface of the object being subjected to the colour-generating treatment at least at the place where the marking is applied, after which the surface of the object is irradiated with laser light in the shape of the marking, the prechrome compounds having been chosen such that and being present in such a concentration that with each wavelength between 400 and 700 nanometers at least part of the amount of incident light is absorbed.

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PROCESS FOR THE MANUFACTURE OF AN OBJECT WITH A COLOURED MARKING

The invention relates to a process for the manufacture of an object with a coloured marking by irradiating the surface of the object with laser light in the shape of the marking.

Such a process is known from WO04/12352. This patent application describes a process in which under randomly chosen conditions the surface of an object is irradiated with laser light, resulting in a marking of an arbitrary colour.

A problem presented by the known process is that the colours that are obtained are not freely chosen, but are obtained randomly. Further, the marking can only be obtained in a limited number of colours. Moreover, it is not possible to obtain a marking on a colourless substrate.

The aim of the invention is to provide a process which does not present the above-mentioned drawbacks.

Surprisingly, this aim is achieved in that at least at the place where the marking is applied the object consists of a plastic composition comprising at least three prechrome compounds which only acquire their colour-generating capacity after a colour-generating treatment and which under the influence of laser light lose their colour-generating capacity, the surface of the object being subjected to the colour-generating treatment at least at the place where the marking is applied, after which the surface of the object is irradiated with laser light in the shape of the marking, the prechrome compounds having been chosen

such that and being present in such a concentration that at each wavelength between 400 and 700 nanometres at least part of the amount of incident light is absorbed.

Due to the use of prechrome compounds which acquire their colour-generating capacity only after a colour-generating treatment it is achieved that the substrate on which the finally resulting marking is formed retains its natural colour. When use is made of colour-generating components which always have a colour-generating capacity, the substrate becomes coloured. That is undesirable. The process according to the invention permits application of markings on a substrate which can have any desired colour. It is also possible for the substrate to have no colour at all.

The prechrome compounds which only acquire their colour-generating capacity after a colour-generating treatment are known to the person skilled in the art. They are compounds which do not acquire a chromatic colour until they have been subjected to a colour-generating treatment, for instance irradiation with UV laser light. Particularly suitable prechrome compounds are the photochrome compounds. These compounds can change colour through a conformation modification and/or a chemical reaction. The conformation modification and/or the chemical reaction is/are achieved through a colour-generating treatment by irradiation with UV light. The colour-generating treatment preferably consists of irradiation of the object with UV laser light. This offers the additional advantage that it is possible to irradiate the object in only the shape of the marking. Most preferably the process according to the invention is characterized in that the colour-generating treatment consists of irradiation with UV laser light, with the number of irradiated photons per cm^2 per second being at least 10^{19}. By UV laser light is understood laser light with a

wavelength of less than 400 nm.

Suitable photochrome compounds are commercially available, for instance from HCH James Robinson Ltd. in the UK. Other suitable prechrome compounds are for instance colouring agents which are encapsulated in microcapsules. These microcapsules are mixed in with the plastic composition and preferably remain intact when the plastic composition is processed to an object, for instance by injection moulding. Such microcapsules acquire their colour-generating capacity by heat being supplied.

The process according to the invention is preferably characterized in that the prechrome compounds are leuco colorants encapsulated in microcapsules and the colour-generating treatment consists of supply of heat. Heat is preferably supplied through irradiation with IR laser light. By IR laser light is understood laser light with a wavelength of more than 700 nm. Leuco colorants are known to the person skilled in the art. They are colorants which as such are colourless, but acquire colour when they are contacted with an electron acceptor by reacting them with a proton. Colorant microcapsules which are suitable for the process according to the invention are described for instance in EP-A-542 133.

The process according to the invention is preferably used on a substrate having a light colour, for instance a white or light-grey colour.

The process according to the invention is preferably characterized in that one or more colours are chosen for the marking, then the wavelength of the laser light is set to a value which depends on the colour chosen and subsequently the surface of the object is irradiated with the laser light.

In this way it is achieved that markings in every or virtually every previously chosen colour can be obtained, simply by selecting the required laser

ight wavelength.

The surface of the object, after it has been subjected to the colour-generating treatment, can for instance be irradiated with a series of different wavelengths, in order in this way to determine a relation between the wavelength of the laser light and the resulting colour of the marking. Then, on the basis of the relationship thus established, the wavelength of the laser light can be set to a value that depends on the selected colour.

The plastic composition may in general contain any thermoplastic or thermosetting plastic or any elastomer. Highly suitable are the plastics which the plastic composition according to WO94/12352 may comprise.

The prechrome compounds preferably are each present in such a concentration that, after the colour-generating treatment, at each wavelength between 400 and 700 nm, at least 20%, more preferably at least 50%, even more preferably at least 80% of the quantity of incident light, expressed in lux, is absorbed.

A person skilled in the art can simply select the prechrome compounds and the concentration and then, after the colour-generating treatment, measure the absorbed light (the absorption spectrum) at each wavelength between 400 and 700 nm by means of one of the known measurement methods and subsequently adapt the prechrome compound and its concentration until the desired absorption spectrum has been obtained.

The process according to the invention can be carried out with the help of one or more laser devices which emit laser light of a wavelength that corresponds to the wavelength value selected on the basis of the desired colour of the marking.

The process according to the invention is preferably carried out with a laser device with adjustable wavelength. This allows easy setting of the

required wavelength, depending on the selected colour of the marking. This also makes it possible to obtain a multicolour marking by means of one device.

The surface of the plastic composition is preferably irradiated with laser light at at least three different wavelengths, more preferably with multiple wavelengths, which depend on the selected colours of the marking. In this way markings are obtained which contain multiple colours and can even come close to or, if a laser beam of a very small diameter is used, actually surpass the quality of a colour photo. Very good results are obtained if the diameter of the laser beam is equal to or smaller than the grain diameter of a colour photo. A typical value for such a grain diameter is 0.5-3 micrometres.

The plastic composition according to the invention preferably only contains prechrome compounds which after the colour-generating treatment under the influence of laser light lose their colour-generating capacity and which after the colour-generating treatment have one single absorption band.

The concept 'absorption band', besides other concepts relevant to the present application, such as 'reflection', is described in Colour Chemistry, 2nd edition, H. Zollinger, VCH Verlag Weinheim, Germany (1991), ISBN 3-527-28352-8.

In this way it is achieved that the wavelength of the colour in which the marking is obtained corresponds to the wavelength of the laser light with which the surface of the plastic composition is irradiated. This makes it very easy to obtain the selected colour, because the selected colour is virtually the same as the colour of the laser light.

The selected colour of the marking is even more similar or even fully similar to the colour of the laser light if after the colour-generating treatment between 400 and 700 nm at each wavelength at least

approximately the same quantity of light is absorbed. Preferably the difference between the quantities of light absorbed at the different wavelengths is not more than 20%, more preferably not more than 10%, still more preferably not more than 5%. The surface of the object prior to application of the marking has a white or light-grey tint at those places where no colour-generating treatment has taken place and a neutral-grey or black tint at those places where the colour-generating treatment has taken place.

Very good results are achieved if the plastic composition contains a first prechrome compound which after the colour-generating treatment reflects light whose principal colour is yellow, a second prechrome compound which after the colour-generating treatment reflects light whose principal colour is magenta and a third prechrome compound which after the colour-generating treatment reflects light whose principal colour is cyan.

Preferably the prechrome compounds after the colour-generating treatment have comparable laser light bleaching efficiency values. By 'bleaching efficiency' is understood the time during which a prechrome compound, after the colour-generating treatment, exposed to irradiation with laser light of a certain intensity, loses 80% of its light absorption capacity, i.e. the quotient of (1 - quantity of reflected light) and the quantity of incident light, both expressed in lux. Preferably the difference in bleaching efficiency between the compounds is not more than 20%, more preferably not more than 10%. In this way it is achieved that if a multicolour marking is applied by means of the process, for each colour only the wavelength of the laser device or laser devices has to be set, while for instance the duration of the treatment and the laser light intensity can simply be the same for each colour.

Further it is important that the prechrome compounds do not or hardly acquire their colour-generating capacity in normal daylight. That is why the prechrome compounds preferably have a colour stability of at least 3, more preferably at least 5 on the Wool scale (according to DIN 54003). Also after the colour-generating treatment the resulting colour-generating components preferably have this colour stability.

Another preferred process is characterized in that at least at the place where the marking is applied the prechrome compounds after the colour-generating treatment each have a maximum in their light absorption spectrum at a different wavelength, with the marking being applied in the form of matrix dots by irradiating the object at place of a matrix dot with laser light of such a wavelength and intensity and during such a length of time that at least one of the prechrome compounds that have acquired their colour-generating capacity after the colour-generating treatment has partially or wholly lost its light absorption capacity.

Thus a marking of any desired colour can be obtained, the marking can have different colours and markings that each have a different colour can be obtained on the surface of the same plastic composition. It is even possible to obtain the marking in many different colours on the surface of the same plastic composition.

This preferred process according to the invention permits application of matrix dots on the surface in a simple manner.

By irradiation with laser light of a certain wavelength the light absorption capacity of a previously selected colour-generating component will be reduced after the colour-generating treatment and at the irradiated spots the surface will reflect the colour that is not absorbed by the component in question. By increasing the intensity of the laser

light or the irradiation time, the brightness of the reflected colour can be enhanced.

By applying a large number of matrix dots on the surface a marking of a desired colour is obtained.

It is also possible to apply differently coloured matrix dots next to each other on the surface. To an observer the colour of the surface at the place of these matrix dots is a mixed colour, because to the eye the colours of the matrix points mix. This manner of blending colours, in which the colours to be mixed are juxtaposed, is called partitive colour blending. The mixed colour is determined by the ratio between the surface areas of the matrix dots and the brightness of the colours in relation to each other. Thus a large number of mixed colours can be formed.

It has to be made sure, however, that the centre-to-centre distance between the dots is small, so that the eye cannot perceive the different matrix dots separately. This colour production technique is also used for newspaper photos.

As is known from colour printing, very good results are obtained if colours are formed by applying matrix dots of at least three different colours on the surface. This is achieved by irradiating the surface with laser light of at least three different wavelengths, at each of which at least one of the light-absorbing components wholly or partially loses its light absorption capacity. In this way it is possible to obtain a large number of other colours from at least three colours by mixing the three colours in the required proportions.

Mixed colours can be obtained in several ways. Thus, mixed colours can be obtained by for instance varying the brightness of the colours of the different matrix dots relative to each other, for instance by irradiating matrix points of a certain colour longer than other matrix points. Another

possibility is to vary the ratio(s) between the total surface areas of the different colours, for instance by making one matrix dot larger than the other or by making more matrix dots of the one colour than of the other colours. The matrix dots can be round or square, but also for instance triangular or bar-shaped, for instance in order to be able to fill up the surface better or to enhance the total reflection of the surface.

A colour can be characterized on the basis of the ASTM E 308 standard, by first measuring the tristimulus values of the colour and deriving from these, as described in said standard, the chromaticity coordinates, which determine the place of the colour in the CIE D65 (10° observer) colour diagram. The colour diagram thus is a graphic representation of all colours in the visible range.

The partitive method of blending yields colours that lie in the colour diagram in the surface between the points that represent the minimally three colours of the matrix points in the colour diagram. These points are the corner points of the surface.

A process according to the invention whereby even more different colours can be obtained is realized if matrix dots are applied wholly or partly overlapping. This method of colour blending is called 'subtractive blending'.

The colour of the surface is preferably generated through subtractive mixing of at least three different coloured matrix dots. The colour range that can be derived from subtractive mixtures is larger than in the case of partitive mixing, because it is also possible to form colours which in the colour diagram lie outside the surface between the points which represent the minimally three different colours of the matrix dots in the colour diagram.

The plastic composition can in principle

comprise any thermosetting or thermoplastic plastic or elastomer. Very suitable are the plastics that can be present in the plastic composition according to WO94/12352.

The prechrome compounds are preferably chosen such that after the colour-generating treatment the surface area between the points representing the minimally three different colours of the matrix dots in the colour diagram is at least equal to 10% of the surface area of the diagram.

Said surface area is preferably equal to at least 30% of the diagram, more preferably at least 75% of the diagram.

The wavelength of the laser light with which the surface should be irradiated in order to cause a selected colour-generating component to lose its light absorption capacity after the colour-generating treatment can simply be determined empirically.

The selected laser light wavelengths for irradiation of the surface preferably are the wavelengths at which the maximum occurs in the absorption spectrum of the colour-generating component which after the colour-generating treatment should lose its light absorption capacity. In this way one obtains a very good selectivity and a good brightness of the colours are ensured.

The process according to the invention is preferably carried out with the help of one or more masks. These masks transmit light at the places where the surface has to be irradiated and do not transmit light where the surface should not be irradiated. By irradiating the surface now with different masks successively with laser light of different wavelengths, matrix dots of different colours can be made on the surface in a rapid and simple way.

An advantage this offers is that the size of the matrix dots is determined by the mask and not by

the diameter of the laser beam, which means that the surface can be irradiated with a laser beam of a large diameter. The irradiation will thus take less time and at the same time a high resolution is achieved.

The process according to the invention is preferably carried out with the help of a variable mask.

By preference, use is made of a mask which is generated by an LCD screen.

Even more preferably, use is made of a PDLCD (Polymer Dispersed Liquid Crystal Display) mask, which offers the additional advantage that it does not absorb the non-transmitted laser beam, but disperses it instead and consequently the mask does not heat up.

Advantages of these masks are that a computer generates the required mask on the LCD or PDLCD screen and the surface can then be irradiated through the mask. Then a second mask can be produced on the screen on the same position. The risk of positioning problems is thus avoided. Another advantage is that it takes very little time to switch from one mask to another.

Very good results are obtained if the process according to the invention is carried out with the help of a laser device which irradiates the surface of the object by means of a sequence of at least three masks on top of each other, each of the masks being irradiated with laser light with each a different wavelength in such a way that the images of the masks are projected on top of each other on the surface of the object. The advantage is that the surface of the object is irradiated with different masks in one go. If the masks are variable this offers the additional advantage that different markings can be applied rapidly in succession. Such an arrangement is known from projection TV.

It is also possible to carry out the process using a moveable laser beam with a variable intensity.

This offers more flexibility in terms of, respectively, the shape of the object to be irradiated and the brightness of the colours.

Further, it is highly advantageous to make use of a laser device with adjustable wavelength, because then it is possible to irradiate the surface with laser light of different wavelengths using a single laser device.

Preferably the laser device is capable of emitting light of the different wavelengths corresponding to the maxima of the absorption spectrums of the different prechrome compounds after the colour-generating treatment. The full range of possible colours can then be produced using a single laser device.

Still more preferably, use is made of a laser device with at least four laser beams of different laser light wavelengths combined in one fibre, with at least one beam having a wavelength of less than 400 nm (UV laser light) and with the possibility of varying the intensity of each beam independently of the other beams. This offers the advantage that the surface of the object can simply be irradiated by means of a single combined laser beam which is capable of activating the prechrome compounds as well as emitting light of all colours. This creates very great flexibility in terms of the range of colours to be chosen from and the shape of the marking to be applied.

The invention also relates to an information carrier which has at least one surface consisting of the above-described plastic composition, that surface being at least 50% covered with one or more markings. Such an information carrier can be provided with a marking by means of the process according to the invention. The marking can contain any desired colour. The marking can even have the shape of a true-to-nature image of for instance objects, animals or persons. The

surface of the information carrier can also be at least 50% covered with text.

Examples of such information carriers are posters, signboards, company nameplates, advertising boards, etc.

The information carrier preferably comprises a supporting layer under the layer made of the plastic composition. This means that the layer made of the plastic composition can be of a minor thickness and that, depending on the type of supporting layer chosen, various kinds of information carrier for a wide variety of purposes are obtained. For instance, the supporting layer may be of paper and the information carrier may have the form of a colour photo or a photocopy. The supporting layer may also consist of a plastic or a metal. Preferably the plastic of the plastic composition is of a type that adheres well to the supporting layer.

The invention also relates to an object that can be made into the above-described information carrier.

Example I

A dry blend was made from 1897 parts by weight of Ronfalin® SFA-34, an acrylonitrile-butadiene-styrene copolymer (ABS) from DSM (Netherlands), 100 parts by weight of Lithophone Silbers® 60% L, a zinc sulphide pigment supplied by Sachtleben (Germany), as well as 0.64 part by weight of Reversacol® Plum Red, 0.32 part by weight of Reversacol® Sea Green and 0.16 part by weight of Reversacol® Corn Yellow, photochrome pigments supplied by HCH James Robinson Ltd. (UK). The dry blend was melted, kneaded at 260°C and processed to granulate using a ZSK® 30 twin-screw kneader from Pfleiderer and Werner (Germany). With the help of an injection moulding machine, type Arburg Allrounder® 320-90-750 the granulate was injection-moulded to

plates measuring 3.2*120*120 mm at a temperature of 240°C. The plates had a light-grey tint.

The plates thus obtained were irradiated with UV laser light (3000 Watts for 5 seconds). The colour of the plates changed from light grey to dark grey during this irradiation. This change of colour was irreversible.

Next, the surfaces of the plates were provided with markings with the help of a laser set-up. A tunable multi-wavelength laser set-up was used (TMW laser set-up). The laser set-up comprised a seeding laser of the type EEO®-355 which was used as a pump laser for an Nd:YAG laser of the type GCR®-230/50. The laser set-up further comprised an optical parameter oscillator (OPO) of the type MOPO® 710, which received the signal from the last-mentioned laser via a frequency doubling optic (FDO) device. The set-up had been supplied by Spectra-Physics (USA).

The following laser settings were chosen:

pulse length: 10 ns
Q-switch frequency: 10 Hz
dot diameter: 8 mm
writing speed: 30 mm/s
line distance: 5 mm

By means of this laser set-up square 20*20 mm markings were made on the surfaces of the sample plates. The wavelength λ of the laser light emitted by the laser set-up was geared to the previously selected colour of the marking. Using a DATA COLOUR® Micro-Flash 200-D reflectometer, supplied by the company DAT COLOUR, the spectrums of the light reflected by the markings were determined. The spectrums appeared to have the shape of a single peak. The wavelengths of the peak maximums (λ_{max}) were determined. The wavelength of the maximum agrees with the colour perceived by the eye. The results are given in table 1. Where the markings had been made the surfaces of the plates had not been

affected as a result of the marking.

TABLE 1

λ_{max} (nm) of reflection spectrums

laser setting	Example I
λ (nm) / colour	
470 / blue	465
530 /green	525
650 / red	655

From the results given in table 1 it appears that the colours of the markings are determined by the wavelength of the laser light. In the dark-grey plate the location of the maxima of the reflection spectrums of the markings (and thus the colour perceived by the eye) agrees with the wavelength of the laser light.

CLAIMS

1. Process for the manufacture of an object with a coloured marking by irradiating the surface of the object with laser light in the form of the marking, wherein at least at the place where the marking is applied the object consists of a plastic composition comprising at least three prechrome compounds which only acquire their colour-generating capacity after a colour-generating treatment and which under the influence of laser light can lose their colour-generating capacity again, the surface of the object being subjected to the colour-generating treatment at least at the place where the marking is applied, after which the surface of the object is irradiated with laser light in the shape of the marking, the prechrome compounds having been chosen such that and being present in such a concentration that with each wavelength between 400 and 700 nanometres at least part of the amount of incident light is absorbed.
2. Process according to claim 1, characterized in that the prechrome compounds are photochrome compounds and the colour-generating treatment consists of irradiation with UV light.
3. Process according to claim 2, characterized in that the colour-generating treatment consists of irradiation with UV laser light, with the number of irradiated photons per cm^2 per second being at least 10^{19}.
4. Process according to claim 1, characterized in that the prechrome compounds are leuco colorants encapsulated in microcapsules and the colour-generating treatment consists of supply of heat.
5. Process according to claim 4, characterized in that the heat is supplied through irradiation with

IR laser light.

6. Process according to any one of claims 1-5, characterized in that one or more colours are chosen for the marking, then the wavelength of the laser light is set to a value which corresponds to the colour chosen and subsequently the surface of the object is irradiated with the laser light.

7. Process according to any one of claims 1-6, characterized in that the process is carried out with a laser device with adjustable wavelength.

8. Process according to any one of claims 1-7, characterized in that the surface of the object is irradiated with laser light with at least three different wavelengths.

9. Process according to any one of claims 1-4, characterized in that between 400 and 700 nanometres the difference between the quantities of light absorbed at different wavelengths is not more than 5%.

10. Process according to any one of claims 1-9, characterized in that the plastic composition contains a first colour-generating component which after the colour-generating treatment reflects light whose principal colour is yellow, a second colour-generating component which after the colour-generating treatment reflects light whose principal colour is magenta and a third colour-generating component which after the colour-generating treatment reflects light whose principal colour is cyan.

11. Process according to any one of claims 1-10, characterized in that the difference between the bleaching efficiency values of the prechrome compounds after the colour-generating treatment is not more than 20%.

12. Process according to any one of claims 1-11, characterized in that the prechrome compounds

after the colour-generating treatment each have a maximum in their light absorption spectrum at a different wavelength, with the marking consisting of matrix dots which are made by irradiating the object at the place of a matrix dot with laser light of such a wavelength and intensity and during such a length of time that at least one of the prechrome compounds after the colour-generating treatment has partially or wholly lost its light absorption capacity.

13. Process according to claim 12, characterized in that the colour of the surface is formed by subtractive blending of the colours of the matrix dots.

14. Process according to claim 12, characterized in that the colour of the surface is formed by partitive blending of the colours of the matrix dots.

15. Process according to any one of claims 12-14, characterized in that the prechrome compounds have been chosen such that the surface area between the points representing the minimally three different colours of the matrix dots in the colour diagram is at least equal to 10% of the surface area of the diagram.

16. Process according to any one of claims 12-15, characterized in that the selected laser light wavelengths for irradiation of the surface are the wavelengths at which the maxima occur in the absorption spectrums of the different prechrome compounds after the colour-generating treatment.

17. Process according to any one of claims 12-16, characterized in that the process according to the invention is carried out with the help of one or more masks.

18. Process according to any one of claims 12-17, characterized in that the process according to the

invention is carried out with the help of a variable mask.

19. Process according to any one of claims 12-18, characterized in that the surface is irradiated with the help of a laser device which irradiates the surface of the object by means of a sequence of at least three masks on top of each other, each of the masks being irradiated with laser light with different wavelengths in such a way that the images of the masks are projected on top of each other on the surface of the object.

20. Information carrier which has at least one surface consisting of the plastic composition as described in claims 1-19, that surface being at least 50% covered with one or more markings.

21. Object that can be made into the information carrier according to claim 20.

INTERNATIONAL SEARCH REPORT

Inte   onal Application No
PCT/NL 97/00608

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/36 B41M5/34 G03C7/46 G03C7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M G03F G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 12352 A (DSM NV ;AAGAARD OLAV MARCUS (NL); DIJK HANS KLAAS VAN (NL); HOEN N) 9 June 1994	1-21
Y	see the whole document	1-4
Y	US 3 892 569 A (SPEERS DANIEL E) 1 July 1975 see the whole document	1,4
Y	DE 41 08 118 A (MITSUBISHI PAPER MILLS LTD) 19 September 1991 see the whole document	1-3
X	US 5 055 373 A (SAEKI KEISO ET AL) 8 October 1991 see the whole document	4

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
29 January 1998	06/02/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rasschaert, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00608

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